Senior Thesis

Geochemistry of Nettle Creek, Champaign County, Ohio

by
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Table of Contents

List of Figures

List of Tables in Appendix

Abstract

Nettle Creek, located in Champaign County Ohio, was sampled on October 1, 1997. The results of the analyzed samples show that the concentrations of major and minor elements are consistent with the Paleozoic carbonate rocks that underlie glacial drift in this area and do not vary significantly downstream with one exception. Sample N-8 has unusually high concentrations of Sr (11,160 ppb), Na (166 ppm), K (10,626 ppb), P (1,120 ppb), Mo (35 ppb), Ni (18 ppb), and Zn (12 ppb). The concentrations of Mg and Ca in this sample are slightly below average. The anomalous chemical composition of sample N-8 is due to the discharge of wastewater from domestic septic systems in Millerstown, which is located close to where sample N-8 was collected. The source of the high Sr concentration in the wastewater could be Sr-rich groundwater recovered in wells by the inhabitants of Millerstown.

Introduction

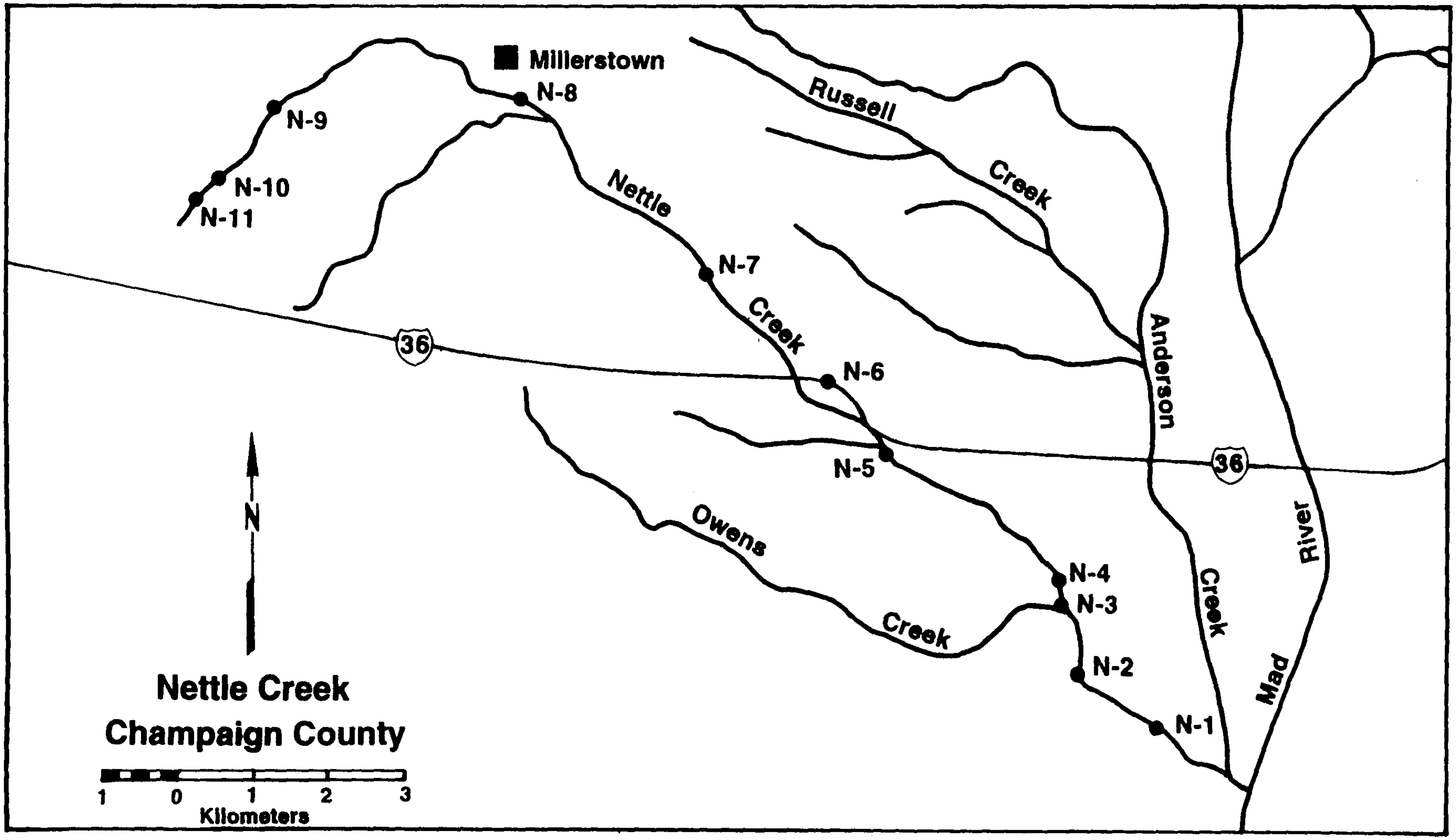
In 1957 Feulner and Hubble collected surface waters as well as groundwater from 22 wells in Champaign County and reported that the Sr concentrations of water samples ranged from 0.0 to 30 ppm. They also sampled seven tributaries of the Mad River and reported that Nettle Creek has the highest concentrations of Sr, perhaps because three springs that flow into Nettle Creek have elevated Sr concentrations of up to 9000 μg/L (Feulner and Hubble, 1960).

The present study was undertaken to confirm the elevated Sr concentrations of Nettle Creek reported by Feulner and Hubble (1960) following the work of Essenburg (1997), who demonstrated the existence of a significant natural Sr anomaly in the surface water of northwestern Ohio centered on the western tributaries of the Scioto River. In addition, this study provides evidence for anthroprogenic contamination of Nettle Creek. Lastly, the dominant minerals reflected in the chemical composition of the water of Nettle Creek are shown to be consistent with the bedrock of the drainage basin.

Methods

On October 1,1997 eleven water samples were collected from Nettle Creek, a tributary of the Mad River in Champaign County in southwestern Ohio. The locations of the samples are indicated in Figure 1. The samples were collected and stored in plastic bottles. The pH of each sample was measured in the laboratory using a Model pHep3 (Hanna Instruments) pH meter. The samples were filtered through acetate filters with a pore size of 0.45μm and acidified by adding two drops of concentrated nitric acid to 250 mL of filtered water. The samples were analyzed by XRAL Laboratories in Toronto,

Figure 1. Map of Nettle Creek showing location of samples collected on October 1, 1997.



Ontario, Canada using inductively coupled plasma spectrometers (ICP). The results, including sensitivity limits, are compiled in Tables 1 and 2 (Appendix). The following elements were below the detection limit: Al (50 ppb), Sc (1 ppb), Ti (10 ppb), V (10 ppb), As (30 ppb), Y (5 ppb), Zr (10 ppb), Cd (10 ppb), Sn (50 ppb), Sb (50 ppb), La (10 ppb), W (50 ppb), Bi (50 ppb).

The concentrations of Sr and Mg in Figures 2 and 3 show good correlation between results reported by Feulner and Hubble (1960) and those collected in 1997. No significant differences exist between the two sets of data, which indicates that the precision and accuracy of the results of this report are as good as those of Feulner and Hubble (1960).

Geology of Nettle Creek

The geology and topography of the drainage basin of Nettle Creek includes Wisconsinan ground and end moraines, outwash deposits and lake sediment underlain by marine carbonate rocks of Ordovician and Silurian age. More specifically, the bedrock of the drainage basin of Nettle Creek consists of the Salina Group, the Lockport Group, and of undifferentiated pre-Lockport rocks of Ordovician age. At the confluence of Nettle Creek and the Mad River, the bedrock consists of undifferentiated Ordovician shale, limestone and dolomite. Traveling further upstream, Ordovician rocks are overlain by Silurian dolomite, limestone, and shale assigned to sub-Lockport strata. The Lockport Dolomite (Lower Silurian) composed of dolomite with minor shale and chert follows upsection. The youngest rocks in the drainage basin of Nettle Creek are the dolomites of

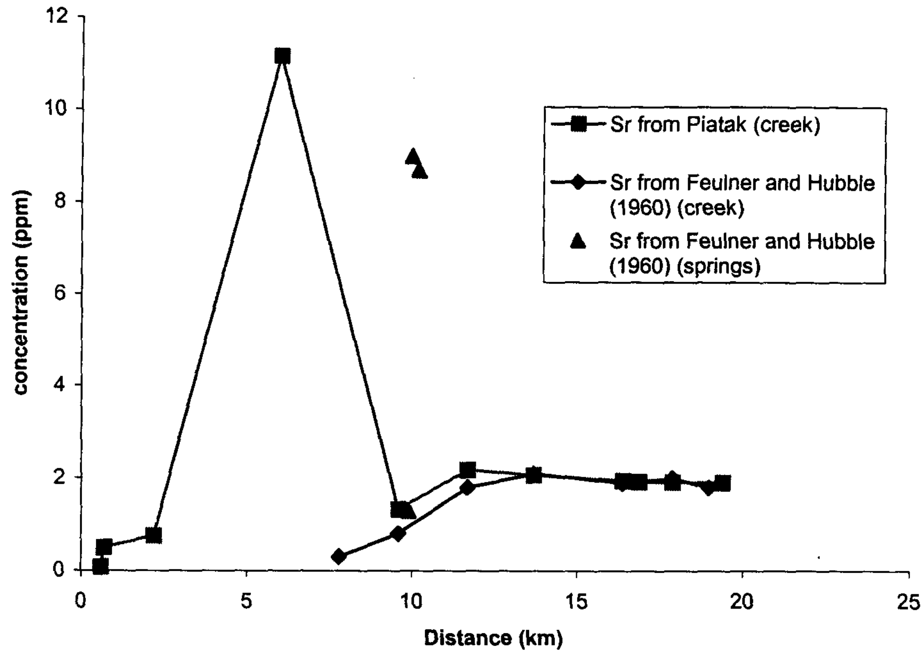


Figure 2. Comparison of Sr concentrations in Nettle Creek as a function of distance downstream

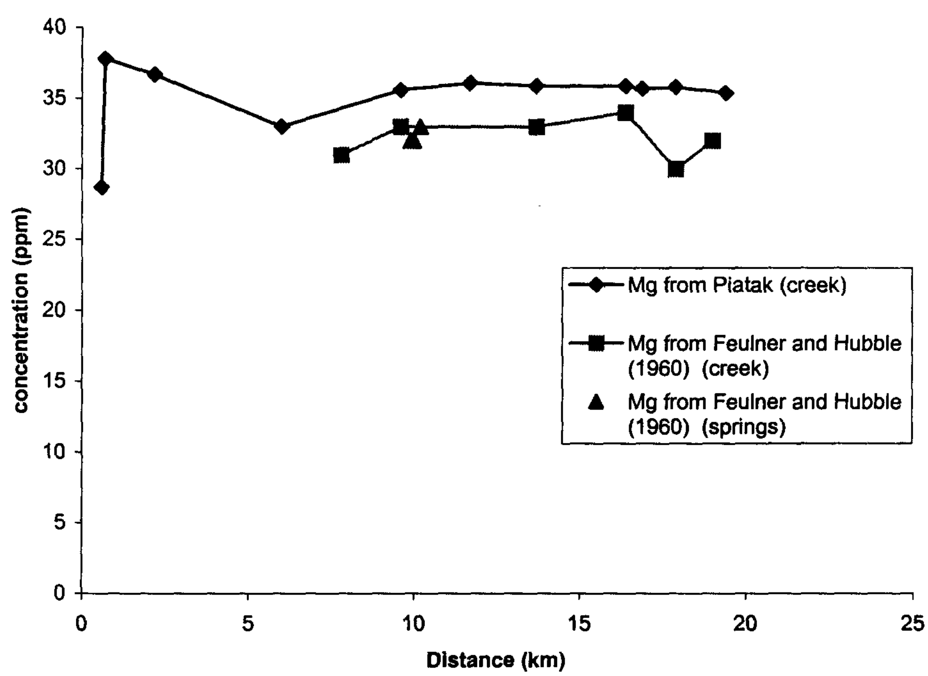


Figure 3. Comparison of Mg concentrations in Nettle Creek as a function of distance downstream

the Salina Group, which occur about 12 kilometers upstream of the confluence. The Salina Group contains layers of salt and anhydrite (Swinford and Slucher, 1995).

Analytical Results

The pH values of the samples in Table 1 vary from 7.0 to 7.8. The most abundant element in the stream is Ca (Figure 4) with an average concentration of 88.1 ppm and a standard deviation of 4.4 ppm for ten samples (excluding N-11). Next in abundance is Mg with an average concentration of 35.8 ±1.2 ppm (excluding N-11). Sample N-11 was field drainage at the head of Nettle Creek and therefore has a distinctly different chemical composition than water farther downstream. The average concentration of Na is 9.0 ±0.3 ppm for eight samples excluding N-11, N-10, and N-8, whose Na concentration deviates significantly from the mean (i.e. N-11: 13.8 ppm; N-10: 61.1 ppm; N-8: 166 ppm). The average concentration of K is 2247 ±269 ppb (excluding N-11, N-10, and N-8 for the same reasons as before). The average Sr concentration of Nettle Creek downstream of site N-8 is 1897 ±269 ppb compared to 11,160 ppb in sample N-8 and only 78 to 755 in samples N-11 to N-9 (Figure 5). The average Ba concentration is 72.1 ±15.4 ppb. Phosphorus in Figure 6 was detected in only two samples, near the source and 6 kilometers downstream. Molybdenum and Ni in Figure 7 were detected only 6 kilometers downstream. The Zn concentrations in Figure 7 are high near the source, 6 kilometers downstream, and near the confluence.

Approximately 6 kilometers from the source, the water in sample N-8 has anomalous concentrations of several elements. The Sr concentration increases from the observed average of about 1.9 ±0.3 to 11.2 ppm as shown in Figure 5. In addition, the

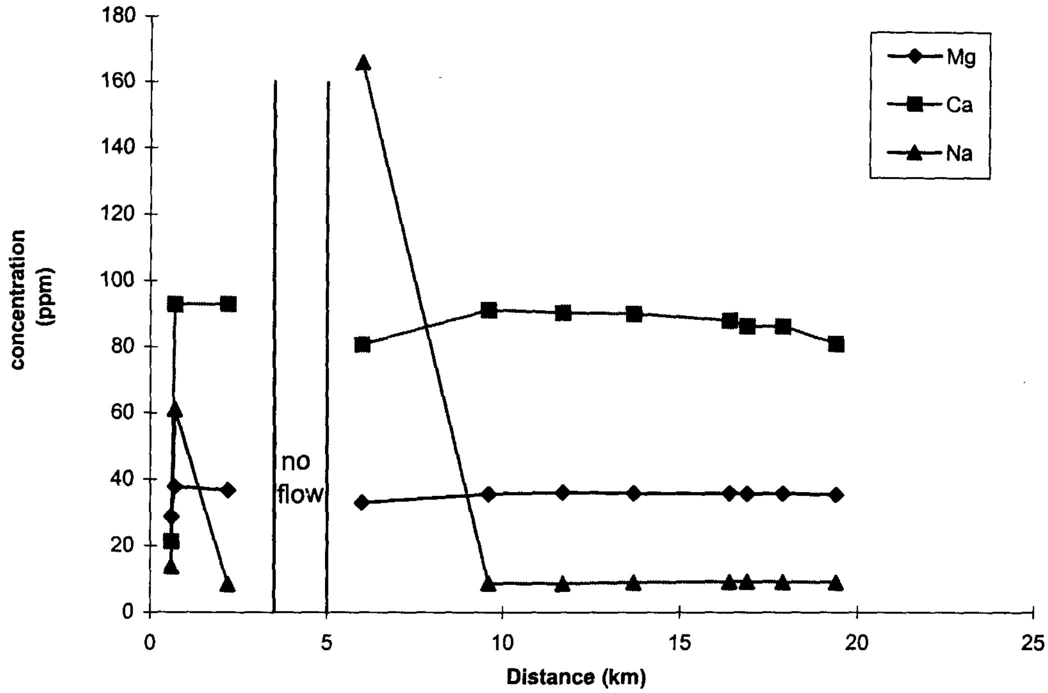


Figure 4. Concentraton of Mg, Ca, and Na in Nettle Creek as a function of distance downstream

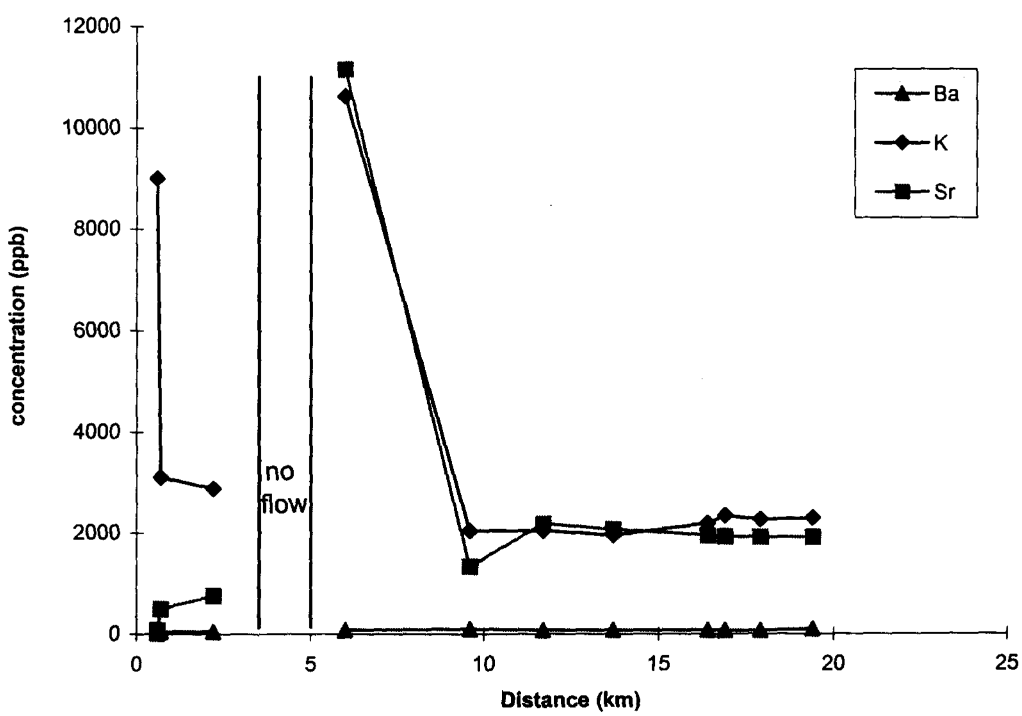


Figure 5. Concentrations of Ba, K, and Sr in Nettle Creek as a function of distance downstream

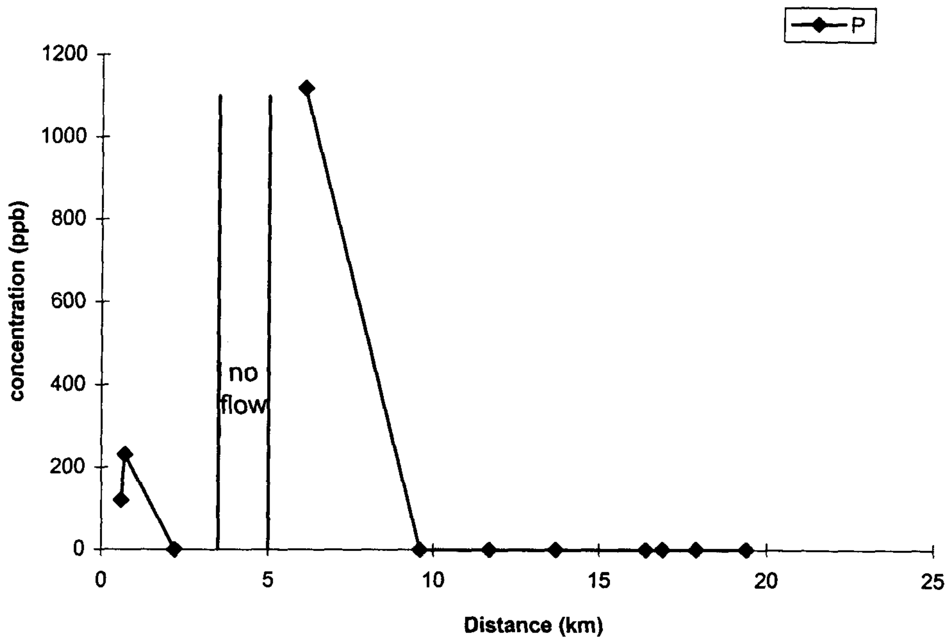


Figure 6. Concentration of P in Nettle Creek as a function of distance downstream

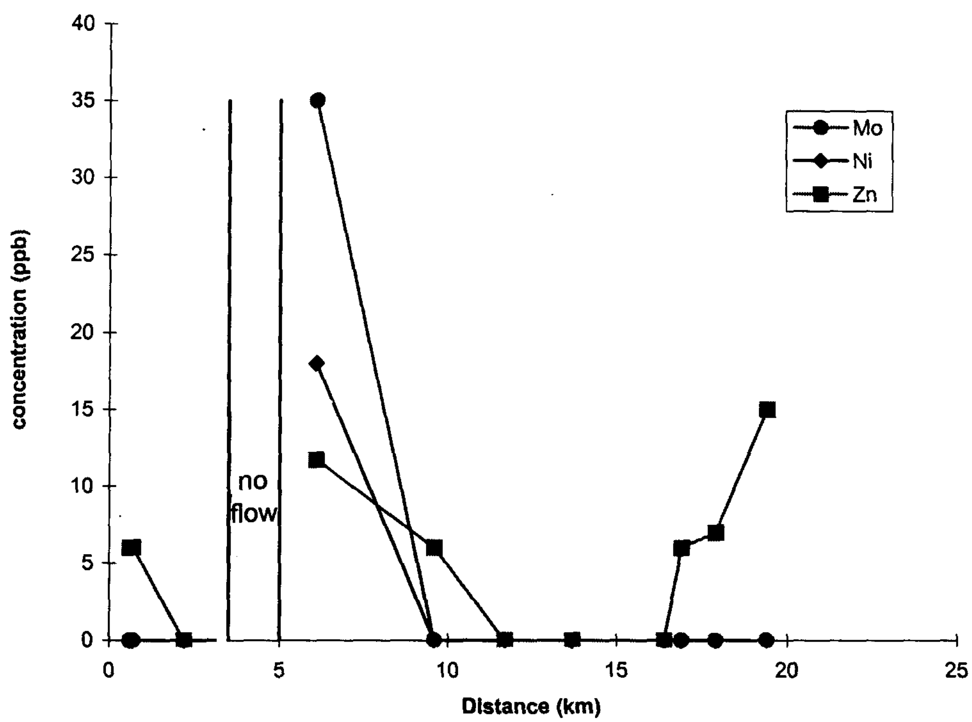


Figure 7. Concentrations of Mo, Ni, and Zn in Nettle Creek as a function of distance downstream

concentrations of K, Na, and P in Figures 4, 5, and 6, all rise by factors of 5 to 19 at this location. On the other hand, the concentrations of Mg and Ca decrease slightly by 8%, respectively, from the averages (Figure 4). The concentrations of Mo, Ni, and Zn in Figure 7 increase, whereas Cr, Mn, Fe, Co, Cu, and Ag do not exhibit unusual concentrations.

The anomalously high Sr concentration of sample N-8 is similar to the concentrations recorded by Feulner and Hubble (1960) in two springs that flow into Nettle Creek with high concentrations of 9.0 ppm and 8.7 ppm as shown in Figure 2. However, the anomalous Sr concentration in sample N-8 cannot be directly compared to the data of Feulner and Hubble (1960) because they did not sample this area of the creek.

Interpretation of Sample N-8

The possible causes of the anomalous concentrations of Sr, Na, K, and P in sample N-8 include mixing of water in Nettle Creek with a brine spring, with industrial effluent, or with municipal wastewater.

The chemical composition of sample N-8 does not match the composition of groundwater in Champaign County in Figure 8 because the concentrations of K and Na in sample N-8 are much higher than those observed in the groundwater. However, the concentrations of Mg and Ca in N-8 are only slightly lower and those of Sr are intermediate between the high and low values in the groundwater. The discrepancies between the concentrations in groundwater in Champaign County and those of sample N-8 indicate that springs supplied by groundwater are an unlikely cause of the anomalous chemical composition of sample N-8.

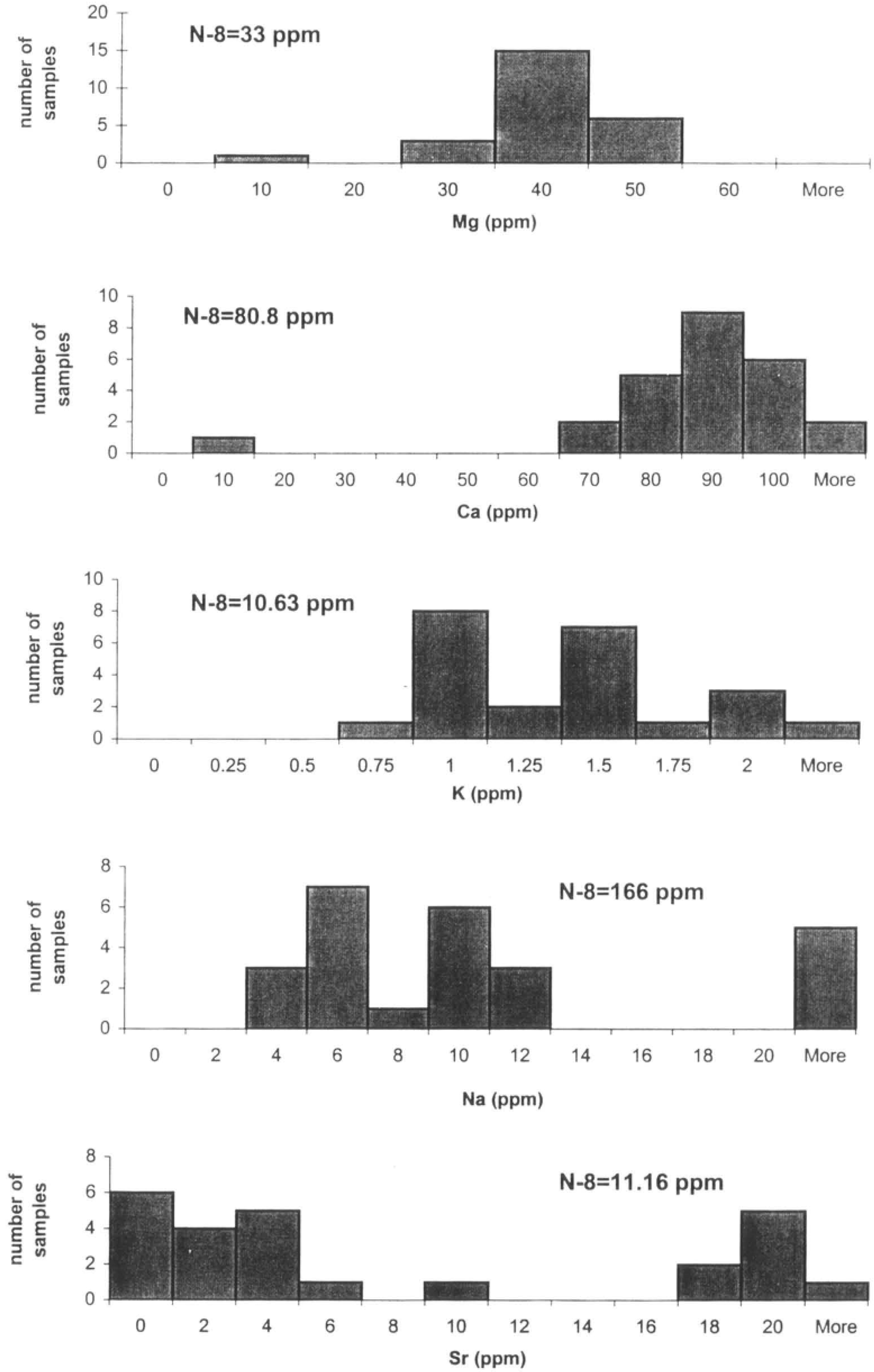


Figure 8. Frequency of elements in groundwater of Champaign County and relative concentration of sample N-8

However, the high Sr concentration of some groundwater in Champaign County permits the conclusion that the elevated Sr concentration of N-8 reflects the presence of Sr-rich groundwater in this area. Also, the concentrations of Mg and Ca reflect the presence of these elements in the groundwater. In that case, the high concentrations of Na, K, and P still remain to be accounted for.

The anomalous concentrations of Na, K, P and some trace metals (Mo, Zn, Ni) may be attributable to the discharge of industrial effluent. However, only two towns exist in the drainage basin of Nettle Creek. Saint Paris lies southwest of the source of Nettle Creek, but does not contribute water to the creek. Millerstown is located 0.4 kilometers from the collecting site of N-8 but no industries are present. Therefore, the anomalous concentrations are not caused by the discharge of industrial wastewater into the creek.

Domestic wastewater discharged by septic tanks is characterized by high concentrations of sodium, chloride, nitrate, and phosphate, which is consistent with the data, whereas the concentrations of Mg, Ca, and Sr reflect the composition of the local groundwater recovered by wells. The Na in wastewater originates from the use of water softeners and table salt used to season food. Potassium and P may be derived from the use of fertilizers and detergents. The high concentrations of Mo and Ni in sample N-8 (Figure 7) are unique because neither is detected in any other part of the stream. The anomalous concentration of Zn may be due to Zn-bearing solder and dissolution of Zn on galvanized steel sheets on roofs and siding. People handling coins and then washing their hands could contribute Ni to wastewater. The source of the Mo is not known.

Overall, the wastewater discharged by Millerstown is characterized by high concentrations of Sr, Na, K, P, Mo, Zn, and Ni. The concentrations of Mg and Ca remain virtually constant.

Relation of Water to Bedrock

The concentrations of elements in Nettle Creek can be directly linked to minerals in the carbonate bedrock that have dissolved in groundwater, which supplies water to the creek. The procedure for making this calculation was developed by Garrels and Mackenzie (1967) based on the assumption that aluminosilicates dissolve incongruently to form kaolinite. Sample MR-1S, collected by Feulner and Hubble in 1957, is used for this calculation in Table 3 (Appendix) because it included the concentration of silicic acid (Feulner and Hubble, 1960). First, concentrations of the ions in mg/L are converted to µmol/L by dividing mg/L by the appropriate gram formula weight and by multiplying by 1000. Next, the analysis is corrected for meteoric precipitation using the composition of average inland rain in the U.S. (Table 21.2, Faure, 1991). A check of the electrical balance among the remaining ions reveals an excess of 76 µeq of positive charge. This imbalance is corrected by increasing HCO_3^- by that amount, therefore increasing the concentration by only 1%. The SiO_2 is then combined with Na^+ and HCO_3^- to form 77 µmol of albite as required by the proportions of ions in Table 4 (Appendix). The remaining Na^+ is combined with Cl^- to make 171 µmol of halite. The Mg^{2+} is then combined with Ca^{2+} and HCO_3^- to form 1272 µmol of dolomite and SO_4^{2-} is combined with the remaining Ca^{2+} to produce 417 µmol of anhydrite. The remaining HCO_3^- is combined with Ca^{2+} to make 150.5 µmol of calcite. The K^+ is then added to NO_3^- to make KNO_3, a common ingredient in fertilizers (Faure, 1991). The amounts of minerals in μmol/L in Table 3 are then converted back into mg/L and then expressed in terms of weight percent.

The results indicate that dolomite, anhydrite, halite, and calcite together contributed 94.3% of the solute. This conclusion is consistent with the geology of the drainage basin of Nettle Creek which is dominantly composed of carbonate rocks of the Salina Group, the Lockport Group, and of undifferentiated Ordovician. The anhydrite and halite solutes are consistent with the occurrence of these minerals in the Salina Group. Only 4.7% of the solute was derived from silicate minerals represented by albite present in the Wisconsinan till that overlies the bedrock and in the shale interbeds within the bedrock. The remaining 1.1% of the solute is assumed to be contributed by various kinds of fertilizers because the drainage basin is actually being farmed.

The elements dissolved in the water of Nettle Creek are released into the water by the dissolution of rocks beneath the surface into the groundwater, which then flows into the creek. Therefore, the dominant minerals reflected in the chemical composition of the water of Nettle Creek are consistent with the bedrock of the drainage basin, which consists of carbonate-evaporite rocks of marine origin.

Conclusion

The results show that the concentrations of major and minor elements in Nettle Creek are consistent with the Paleozoic carbonate rocks that underlie glacial material in this area. The concentrations do not vary significantly downstream with one exception. Sample N-8 displays unusually high concentrations of Sr, Na, K, P, Mo, Ni, and Zn which are contributed by the discharge of wastewater from domestic septic systems in Millerstown, located close to where the sample was collected. The wastewater is characterized by high Sr, Na, K, P, Mo, Ni and Zn and near average Mg and Ca concentrations. The source of the high Sr concentration in the wastewater could be due to Sr-rich groundwater recovered in wells by the inhabitants of Millerstown.

Acknowledgments

I would like to express my appreciation to Dr. Gunter Faure who supervised and suggested this project. His generous allocation of time and resources enabled me to learn about the geochemistry of stream water as well as groundwater. I learned a great deal as well as enjoyed every minute of our conversations.

The Geochemical Support Fund provided the funds for the samples to be analyzed by XRAL Laboratories using inductively coupled plasma spectrometers.

References Cited

Essenburg, C. L., 1997, Sr/Ca ratios in surface water of mid-western U.S.A. and Canada: unpublished masters thesis, Department of Geological Sciences, The Ohio State University.

Faure, G., 1991. Principles and Application of Inorganic Geochemistry: Prentice Hall Inc., New Jersey.

Feulner, A. J., and Hubble, J. H., 1960. Occurrence of strontium in the surface and ground waters of Champaign County, Ohio: U.S. Geological Survey,55:176-186.

Garrels, R. M., and Mackenzie, F. T., 1967. Origin of chemical composition of some springs and lakes: W. Stumm (Ed.), Equilibrium Concepts in Natural Water Systems. Advances in Chemisty Series. No. 67, Amer. Chem. Soc., Washington, DC.

Swinford, E. M., and Slucher, E. R., 1995. Regional Bedrock Geology of the Bellefontaine, Ohio, 30x60 Minute Quadrangle: Ohio Division of Natural Resources, Division of Geological Survey.

Appendix

Table 1. Major element concentrations from Nettle Creek collected on October 1, 1997

	distance downstream (km)	pH	Mg (ppm)	Na (ppm)	K (ppb)	Ca (ppm)	Sr (ppb)	Ba (ppb)
Detection			0.05	0.05	100	0.05	1	10
N-1	19.4	7.8	35.4	9.06	2289	81.2	1909	94
N-2	17.9	7.3	35.8	9.15	2263	86.5	1916	69
N-3	16.9	7.2	35.7	9.21	2339	86.5	1926	68
N-4	16.4	7.2	35.9	9.27	2187	88.2	1950	74
N-5	13.7	7.2	35.9	9.06	1950	90.2	2067	73
N-6	11.7	7.1	36.1	8.62	2043	90.5	2184	76
N-7	9.6	7	35.6	8.75	2035	91.3	1331	94
N-8	6	7.6	33.0	166	10626	80.8	11160	76
N-9	2.2	7.1	36.7	8.48	2872	92.9	755	47
N-10	0.7	7.1	37.8	61.1	3100	92.8	499	50
N-11	0.6	7.8	28.7	13.8	9003	21.3	78	13

Table 2. Minor element concentrations from Nettle Creek collected on October 1, 1997

	P(ppb)	Cr(ppb)	Mn(ppb)	Fe(ppb)	Co(ppb)	Ni(ppb)	Cu(ppb)	Zn(ppb)	Mo(ppb)	Ag(ppb)
Detection	50	10	5	50	10	10	5	5	10	1
N-1	-(1.)	-	-	-	11	-	-	15	-	3
N-2	-	-	-	-	-	-	5	7	-	2
N-3	-	-	-	-	-	-	-	6	-	3
N-4	-	-	-	-	22	-	-	-	-	3
N-5	-	-	-	-	12	-	-	-	-	-
N-6	-	16	-	-	-	-	5	-	-	1
N-7	-	-	16	-	-	-	5	6	-	5
N-8	1120	-	-	-	-	18	6	12	35	5
N-9	-	-	-	-	-	-	-	-	-	-
N-10	231	-	-	-	-	-	-	6	-	-
N-11	120	12	7	181	-	-	-	6	-	1

(1.) "-" means not detected

Table 3. Deviation of weight percent of rocks contributing ions to Nettle Creek

Sample MR-1S	SiO_2	Ca 2+	Mg 2+	Sr 2+	Na +	K +	HCO_3 -	SO_4(2-)	Cl -	F -	NO_3 -	mineral (umol)
mg/L = ppm	9.4	76	31	1.6	6.1	2	329	43	8.5	0.2	4.7	
gram formula wt.	60.09	40.08	24.305	87.62	22.99	39.1	61.02	96.06	35.45	19	62.01	
umol/L	154	1896	1276	18	265	51	5392	448	240	11	76	
rain inland U.S. mg/L	0	1.4	0.1	0	0.4	0.2	0	3	0.41	0	1.2	
rain umol/L	0	35	4	0	17	5	2	31	12	0	19	
net umol/L	154	1861	1272	18	248	46	5390	417	228	11	57	
electrical neutrality	154	1861	1272	18	248	46	5466	417	228	11	57	
albite	0	1861	1272	18	171	46	5389	417	228	11	57	77
halite	0	1861	1272	18	0	46	5389	417	57	11	57	171
dolomite	0	589	0	18	0	46	301	417	57	11	57	1272
anhydrite	0	172	0	18	0	46	301	0	57	11	57	417
calcite	0	21.5	0	18	0	46	0	0	57	11	57	150.5
KNO_3	0	21.5	0	18	0	0	0	0	57	11	11	46
total leftover	0	21.5	0	18	0	0	0	0	57	11	11	

	umol/L	mg/L	weight %
dolomite	1272	234.6	54.4
halite	171	99.9	23.2
anhydrite	417	56.8	13.2
albite	77	20.2	4.7
calcite	150.5	15.1	3.5
KNO_3	46	4.7	1.1
totals		431.3	100.1

Table 4. Number of moles of ions released into solution per mole of mineral (adapted from Table 21.4, Faure, 1991)

Mineral	Na^+	K^+	Mg^{2+}	Ca^{2+}	SiO_2	HCO_3^-	SO_4^{2-}
Albite,	1	0	0	0	2	1	0
Anorthite	0	0	0	1	0	2	0
Orthoclase	0	1	0	0	2	1	0
Biotite	0	1	2	0	2	5	0
Pyroxene	0	0	1	1	1	4	0
Enstatite	0	0	1	0	1	2	0
Diopside	0	0	1	1	2	4	0
Calcite	0	0	0	1	0	2	0
Dolomite	0	0	1	1	0	4	0
Gypsum	0	0	0	1	0	0	1
Pyrite	0	0	0	0	0	0	2